3. G. I. Migachev, N. G. Grekhova, and A. M. Terent'ev, Khim. Geterotsikl. Soedin., No. 3, 388 (1981).
4. G. I. Migachev and N. G. Grekhova, Zh. Vses. Khim. Ova., 26, 213 (1981).
5. B. E. Zaitsev and Yu. N. Sheinker, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 11, 2070 (1962).
6. B. Penfold, Acta Crystallogr., No. 6, 591 (1953).
7. A. S. P. Smith, J. Am. Chem. Soc., 70, 320 (1948).
8. M. Dewar, Molecular Orbital Theory in Organic Chemistry [Russian translation], Mir, Moscow (1972), p. 183.
9. G. I. Kagan, V. A. Kosobutskii, V. K. Belyakov, and O. G. Tarakanov, Khim. Geterotsikl. Soedin., No. 6, 794 (1972).
10. K. Nishimoto and L. S. Forster, Theor. Chim. Acta, 3, 407 (1965).

SYNTHESIS OF ISOMERIC SPIRO[AZAFLUORENEOXIRANES] FROM 3-METHYL-2-AZAFLUORENE AND 4-AZAFLUORENE

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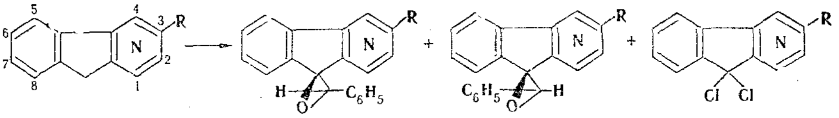
Compounds that belong to the class of new spiran heterocyclic systems that contain azafluorene and oxirane fragments were obtained from the corresponding azafluorenes and benzaldehyde under interphase-catalysis conditions. The Z and E isomers of 3-methyl-3'-phenylspiro(2-azafluorene-9,2'-oxirane) and 3'-phenylspiro(4-azafluorene-9,2'-oxirane) were isolated, and their configurations were established by NMR spectroscopy.

It has been established by means of the PMR spectra that 3'-phenylspiro[fluorene-9,2'-oxirane], which could not be isolated since it is converted to 9-methoxy-9-(α-hydroxybenzyl)-fluorene during crystallization from methanol, is formed in the reaction of fluorene with benzaldehyde, carbon tetrachloride, and 50% aqueous sodium hydroxide in the presence of triethylbenzylammonium chloride (TEBA) — reaction under interphase-catalysis (IPC) conditions [1].

We subjected 3-methyl-2-azafluorene (I) and 4-azafluorene (II) to a similar reaction. In the case of conversion of these heterocyclic compounds to stable spirans with azafluorene and oxirane fragments one had to expect the formation of compounds that are isomeric with respect to the position of the phenyl substituent in the oxirane ring relative to the pyridine ring of the azafluorene fragment.

3-Methyl-3'-phenylspiro[2-azafluorene-9,2'-oxirane] (III) was obtained from I in 25% yield. Its Z (IIIa) and E (IIIb) isomers were isolated by chromatography. The Z (IVa) and E (IVb) isomers of 3'-phenylspiro[4-aza-fluorene-9,2'-oxirane] were obtained from 4-azafluorene (II) in an overall yield of more than 50%. Spiro compounds III and IV are stable crystalline substances and were purified by crystallization from heptane.



I, II   III-IVa   III-IVb   V, VI

I, III, V — 2-aza, $R=CH_3$; II, IV, VI — 4-aza, R=H

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The configurations of the isomeric compounds of III and IV were established on the basis of data from the PMR spectra. The closeness of the 1-H protons in the Z isomers (IIIa and IVa) and the 8-H protons in the E isomers (IIIb and IVb) to the phenyl group of the oxirane ring as a consequence of the magnetic anisotropy of this substituent gives rise to an ~1 ppm shift of their signals to strong field, and the spectra of the Z and E isomers in the aromatic region have completely different forms. In the case of the Z isomer (IIIa) the 1-H signal has a shift of 7.53 ppm and is overlapped with the signals of the protons of the phenylene ring, whereas in the case of the E isomer (IIIb) the 8-H (6.53 ppm) and 7-H (7.04 ppm) signals are shifted to strong field, while the signal of the α proton (1-H) has its usual shift of 8.52 ppm. The same regularity is also observed for the Z and E isomers of 3'-phenylspiro[4-azafluorene-9,2'-oxirane] (IV): In the case of the Z isomer (IVa) the 1-H signal is found at 6.77 ppm, while the 8-H signal (7.4-7.6 ppm) is overlapped by the signals of the phenyl substituent; in the case of the E isomer (IVb) the 1-H signal is found at 7.63 ppm, while the 8-H signal is found at 6.53 ppm. Such large differences made it possible to establish the configurations unambiguously.

In the reactions that we carried out we also isolated 3-methyl-9,9-dichloro-4-azafluorene (V) and 9,9-dichloro-4-azafluorene (VI) in 4 and 10% yields, respectively.

The formation of oxiranes from CH acids under interphase-catalysis (IPC) conditions in the presence of carbon tetrachloride includes a step involving prior chlorination [2], after which the monochloro derivative reacts with the aldehyde much in the same way as in the Darzens reaction [1]. In the case of azafluorenes the reaction proceeds in part to favor the formation of dichloro derivatives V and VI. It has been previously established that 9-bromo-4-azafluorene is readily formed when azafluorene II is treated with N-bromosuccinimide (NBS), whereas in the presence of bases it is converted to bis(4-azafluorenylidene) (VIII) [3]. The latter was isolated in very small amounts in the synthesis of spiro compound IV, whereas its analog — bis(3-methyl-2-azafluorenylidene) (VII) — was isolated in the synthesis of III.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were obtained with Brucker WP-80 and Tesla BS-497 spectrometers at 80 and 100 MHz, respectively, with tetramethylsilane as the internal standard. In the analysis of the spectra we used the ITRCAL iteration program. The mass spectra were recorded with an MKh-1303 spectrometer at an ionizing voltage of 70 eV. Thin-layer chromatography (TLC) was carried out on activity II aluminum oxide in an ether—heptane system (1:1).

3-Methyl-3'-phenylspiro[2-azafluorene-9,2-ozirane] (III). A mixture of 2 g (11 mmole) of azafluorene I, 6 ml of 50% aqueous sodium hydroxide solution, 1.5 g (14 mmole) of benzaldehyde, and 28 mg of TEBA in 6 ml of carbon tetrachloride was stirred at 10°C for 4 h (the experiment was carried out in a stream of nitrogen). Water (20 ml) was added, and the organic layer was separated. The reaction products were extracted from the aqueous layer with carbon tetrachloride. The solvent was removed from the extract, and the residue (2.65 g) was separated chromatographically on aluminum oxide [heptane—ether (6:1)] to give 0.12 g (4%) of colorless crystals of dichloride V with mp 153-155°C (from heptane) and R_f 0.85. PMR spectrum: 8.78 (1H, s, 1-H), 7.45-7.9 (5H, m, aromatic protons), and 2.75 ppm (3H, s, 3-CH_3). Found: Cl 28.4; N 5.7%; M^+ 249. $C_{13}H_9Cl_2N$. Calculated: Cl 28.5; N 5.7%; M 249. Subsequent elution gave 0.6 g (19%) of colorless crystals of spiro compound IIIa with mp 155-158°C (from heptane) and R_f 0.82. PMR spectrum: 7.53 (1H, s, 1-H), 7.0-7.2 (9H, m; the phenyl protons of the substituent covered up the signals of the 4-H, 5-H, 6-H, and 7-H protons), 7.6 (m, 8-H), 5.13 (1H, s, 3'-H), and 2.65 ppm (3H, s, 3-CH_3). Found: C 84.5; H 5.5; N 5.2%; M^+ 285. $C_{20}H_{15}NO$. Calculated: C 84.2; H 5.3; N 4.9%; M 285. The chromatographic separation of the mixture ultimately gave 0.22 g (7%) of spiro compound IIIb as colorless crystals with mp 143-147°C (from heptane) and R_f 0.7. PMR spectrum: 8.52 (1H, s, 1-H), 7.4-7.5 (6H, m; the signals of the protons of the phenyl substituent covered up the 4-H signal), 5.01 (1H, s, 3'-H), and 2.75 ppm (3H, s, 3-CH_3. The phenylene protons, which gave an ABCD spectrum, had the following values according to calculations by means of the ITRCAL program: 7.70 (5-H), 7.34 (6-H), and 6.53 ppm (8-H); $J_{5,6,6,7,7,8}$ = 7.5, $J_{5,7,6,8}$ = 1.3, and $J_{5,8}$ = 0.7 Hz. Found: C 84.3; H 5.2; N 4.8%; M^+ 285. $C_{20}H_{15}NO$. Calculated: C 84.2; H 5.3; N 4.9%; M 285. Dimer VII [0.05 g (1.3%)] was also isolated and had R_f 0.1. Found: M^+ 358. $C_{26}H_{18}N_2$. Calculated: M 358.

3'-Phenylspiro[4-azafluorene-9,2'-oxirane] (IV). A 1-g (5.9 mmole) sample of azafluorene II, 7.5 ml of 50% sodium hydroxide solution, 0.9 g (8.4 mmole) of benzaldehyde, 40 mg of TEBA, and 10 ml of carbon tetrachloride were used for the reaction. The reaction and the isolation of the products were carried out as in the preceding experiment to give 0.14 g (10%) of dichloride VI as colorless crystals with mp 139-140°C (from heptane) and R_f 0.6. Found: Cl 28.1; N 5.3%; M^+ 235. $C_{12}H_7Cl_2N$. Calculated: Cl 29.4; N 6.0%; M 235. Spiro compound IVa [0.45 g (28%)] was also obtained and had mp 123-124°C (from heptane) and R_f 0.52. PMR spectrum: 8.06 (m, 5-H), 7.4-7.6 (the signals of the phenyl substituent covered up the signals of the 6-H, 7-H, and 8-H protons), and 4.97 ppm (1H, s, 3'-H). The protons of the pyridine ring, which give an ABC spectrum, were calculated by means of the ITRCAL method and had the following values: 6.77 (1-H), 6.81 (2-H), and 8.48 ppm (3-H); $J_{1,2} = 7.8$, $J_{1,3} = 1.2$, and $J_{2,3} = 5.7$ Hz. Found: C 84.4; H 4.8; N 5.2%; M^+ 271. $C_{19}H_{13}NO$. Calculated: C 84.2; H 4.9; N 5.2%; M 271. Chromatography ultimately yielded 0.44 g (27.7%) of spiro compound IVb in the form of colorless crystals with mp 163.5-165°C (from heptane) and R_f 0.4. PMR spectrum: 4.95 (1H, s, 3'-H). The protons of the pyridine ring, which give an ABC spectrum, were calculated by means of the ITRCAL method and had the following values: 7.63 (1-H), 7.18 (2-H), and 8.60 ppm (3-H); $J_{1,2} = 7.5$, $J_{1,3} = 1.5$, $J_{2,3} = 5.0$ Hz. The protons of the phenylene ring, which give an ABCD spectrum, were calculated by means of the ITRCAL method and had the following values: 7.98 (5-H), 7.36 (6-H), 7.01 (7-H), and 6.53 ppm (8-H); $J_{5,6} = 7.6$, $J_{5,7} = 1.3$, $J_{5,8} = 0.7$, $J_{6,7} = 7.5$, $J_{6,8} = 1.1$, and $J_{7,8} = 7.5$ Hz. Found: C 84.3; H 5.1; N 5.2%; M^+ 271. $C_{19}H_{13}NO$. Calculated: C 84.2; H 4.9; N 5.2%; M 271. Dimer VIII [0.01 g (0.52%)] was also isolated. Found: M^+ 330. $C_{24}H_{14}N_2$. Calculated: M 330.

LITERATURE CITED

1. A. Janczyk, A. Kwast, and M. Makosza, J. Org. Chem., 44, 1192 (1979).
2. M. Makosza, B. Serafin, and I. Gajos, Roczn. Chem., 43, 671 (1969).
3. N. S. Prostakov, Rafael Vasquez Ismael, N. M. Mikhailova, and B. N. Anisimov, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 22, 920 (1979).

N-OXIDES OF 2- AND 4-AZAFLUORENONES AND NITRO DERIVATIVES OF 2- and 4-AZAFLUORENES

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It was demonstrated by PMR spectroscopy that mixtures of N-oxides of 6- and 7-nitro derivatives are formed in the nitration of the N-oxides of 3-methyl-2- and 4-azafluorenes. The products were deoxygenated to give nitro derivatives of 2- and 4-azafluorenes. The N-oxides of nitro-substituted azafluorenes were converted to salts of the aci forms by the action of alkali.

Information regarding the N-oxides of azafluorenes is limited to two communications [1, 2]. We obtained N-oxides I and II from the recently accessible 3-methyl-2-aza- and 4-azafluorenes, which are obtained by catalytic dehydrocyclization of, respectively, 2,5-dimethyl-4-phenyl- and 3-methyl-2-phenylpyridines [1, 3]. The N-oxides of 3-methyl-2-aza- (III) and 4-azafluorenone (IV) were obtained in rather high yields in the oxidation of N-oxides I and II with potassium permanganate in the presence of ammonium nitrate.

In the present communication we present the results of experiments on the nitration of N-oxides of azafluorenes and the transformations to nitro derivatives under the influence of bases. In the first case it was necessary to solve the problem of the orientation in the electrophilic substitution of these heterocyclic systems. Since the position of the nitro group and the isomeric composition of the nitration products were determined from the PMR spectra, for comparison we investigated the PMR spectra of the starting N-oxides and the prod-

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